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Plasma surface functionalization and dyeing kinetics of Pan-Pmma copolymers

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ABSTRACT

Fiber surface modification with air corona plasma has been studied through dyeing kinetics under isothermal conditions at 30 °C on an acrylic-fiber fabric with a cationic dye (CI Basic Blue 3) analyzing the absorption, desorption and fixing on the surface of molecules having defined cationic character.

The initial dyeing rate in the first 60 s indicates an increase of 58.3% in the dyeing rate due to the effect of corona plasma on the acrylic fiber surface. At the end of the dyeing process, the plasma-treated fabrics absorb 24.7% more dye, and the K/S value of the acrylic fabric increases by 8.8%. With selected dyestuff molecules, new techniques can be designed to amplify the knowledge about plasma-treated surface modifications of macromolecules.

1. Introduction

High added value products are produced in the world with acrylic fibers for applications in the technical textiles field, due to its versatility and proven resistance to ultraviolet radiation, acids and alkalis, and microorganisms. Acrylic fibers are random copolymers composed at least of 85% by weight of acrylonitrile (AN) units. The remaining <15% consists of neutral and/or ionic co-monomers which are added to improve the properties of the fibers. Neutral co-monomers like methyl acrylate (MA), vinyl acetate (VA), or methyl methacrylate (MMA) are used to modify the solubility behavior of the acrylic copolymers in the spinning solvents, to modify the acrylic fiber morphology, and to improve the rate of diffusion of dyes into the acrylic fiber and other processing properties [1–3]. Acrylic fibres vary widely in their dyeability because of the different amounts of the different co-monomers used with poly(acrylonitrile) that modify the fibres' glass transition temperature (T_g). This may range from 70–95 °C according to the source of the acrylic fibre manufacturer [4,5].

Basic dyes are cationic dyes characterized by their affinity for standard acrylic, modacrylic, basic-dyeable polyester and basic-dyeable nylon fibres [6]. Cationic dyes are suitable for the dyeing of acrylic and modacrylic fibres, on which basic dyes can impart bright colors with considerable brilliance or fluorescence. The ionic attraction between the basic dye and the terminal sulphonic acid specific dyesites in acrylic fibres is strong, which yields high color fastness to washing. The close-packed physicochemical nature of acrylic fibers and the strong dye-fibre bonding can result in poor migration and leveling properties during dye application [5,7,8].

Physical and chemical properties of a polymer surface significantly affect adhesion, wetting properties, friction, and light reflection. Low-temperature plasma treatment is of interest as an effective technique for modifying polymer surfaces [9–15]. Plasma techniques are of scientific interest for several reasons: they allow modification of the surface layers up to a depth of several nanometers of the polymer substrate while maintaining its bulk properties. They can achieve the desired surface polarities and their low temperature avoids sample destruction. As a result of the plasma treatment, the surface may be functionalized (generating new chemical groups), and/or degraded as a result of the etching effect (removal of surface material), [16] whereas the bulk properties remain intact. Plasma technology is well known as environmentally friendly for imparting functional finishes to textile materials without the use of harmful chemicals or water consumption.

The effects of plasma on different textiles have been extensively studied, particularly with regards to the improved wettability of

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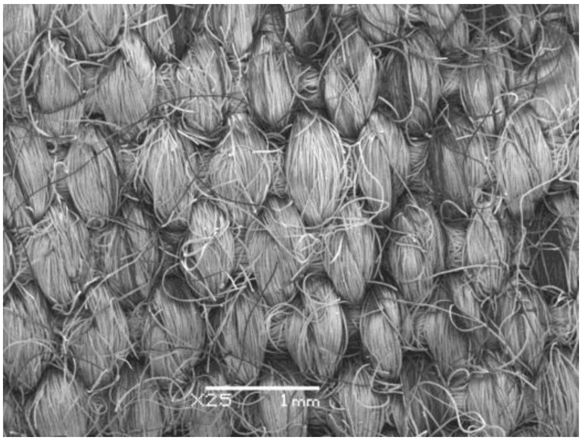

Fig. 1. Acrylic fabric used for the experiment.

fibers such as wool, polyamide or polypropylene [17–19] which is closely related to their improved dyeability. Plasma treatment has been applied to acrylic fibers and films to achieve the modification of physical properties of the surface of the acrylic fibers [20,21]. The modification of the surface characteristics and antistatic behavior of acrylic fibers [22], to perform the plasma-induced graft polymerization with acrylic acid [23–25] or to improve by atmospheric plasma treatment the durability of a water and oil repellent finishing for acrylic fabrics [26] have also been studied. By means of selected dyestuff molecules, knowledge on plasma effects on polymeric surfaces can be enhanced.

The purpose of this study is to compare the kinetic behavior of the dyeing process at temperatures below the T_g, between untreated and corona plasma-treated acrylic fabrics. Corona plasma has the advantage of operating at atmospheric pressure, thus allowing potential insertion of the plasma process in the industrial textile finishing chain. This treatment is expected to increase the wetting properties of the fabric to improve surface cleaning by etching effects, and to modify the physical and chemical properties

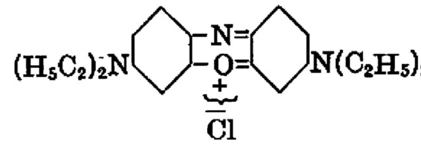

Fig. 3. Chemical structure of the CI Basic Blue 3 dyestuff.

of the surface mainly by functionalization with new hydrophilic moieties. Thus, after surface characterization of the materials, in the present work it is evaluated how much dyestuff is attached to the fabric in the beginning, and at the end of an isothermal 18 h dyeing process for both acrylic fabric. A subsequent washing of the untreated and plasma-treated dyed acrylic fabrics will also be performed to quantify how much dye is removed after a soaping process to evaluate the fixation degree of the dyestuff on the acrylic fiber.

2. Experimental

2.1. Material

An acrylic weaved fabric has been selected (supplied by *SATI S.A.*, Spain), with closed laminar structure, industrially-prepared for dyeing, which is a base product for manufacture of technical textiles. This acrylic fabric (Fig. 1) is 0.65 mm thick and has a weight by square meter of 283.5 g/m^2 with warp density of 30 yarns/cm and weft density of 14 yarns/cm. The warp and weft yarns count is of 59.5 tex/2c and 58.6 tex/2c, respectively. The FTIR spectrum of this acrylic fabric, shown in Fig. 2, has allowed determining PAN/PMMA as copolymer [27]. The surface structure corresponds to acrylic fibers model "long striations" Fig. 3.

The cationic dye used for this experiment was Nitrosate N, N-diethyl-m-anisidine (CI Basic Blue 3, 51004, DyStar). CI Basic Blue 3 (Astrazon Blue BG) dye was blended with glacial acetic acid, adding hot water and finally filtered to avoid clumping in the solution.

Laventín EE-BL (*BASF Curtex S.A.*, Spain) was used for the laboratory washing processes of the acrylic fabrics. It is a nonionic

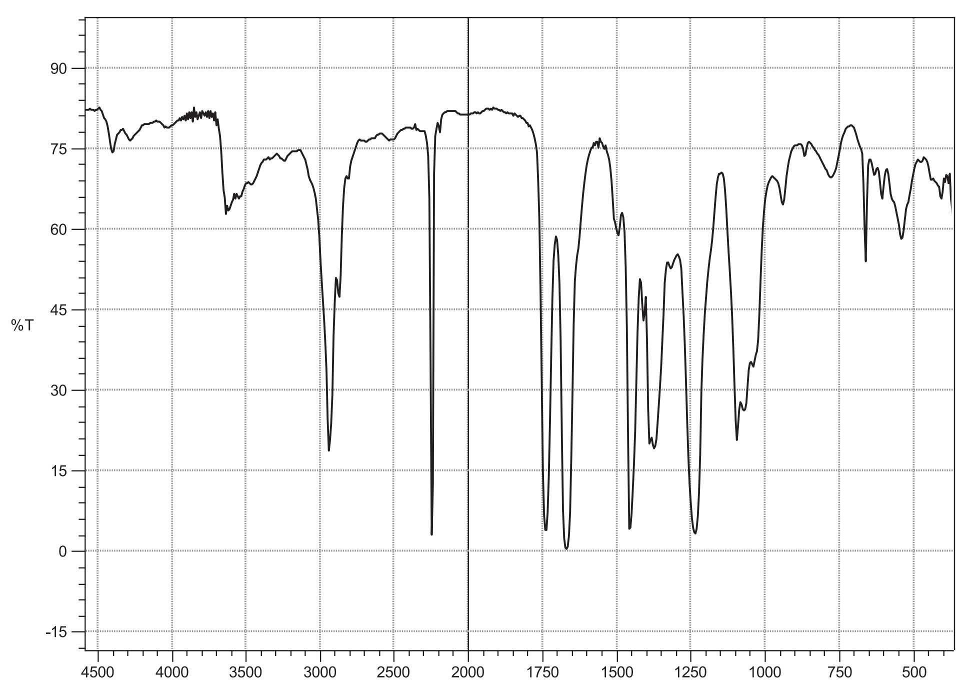

Fig. 2. FT-IR spectra of the acrylic fiber (PAN/PMMA copolymer).

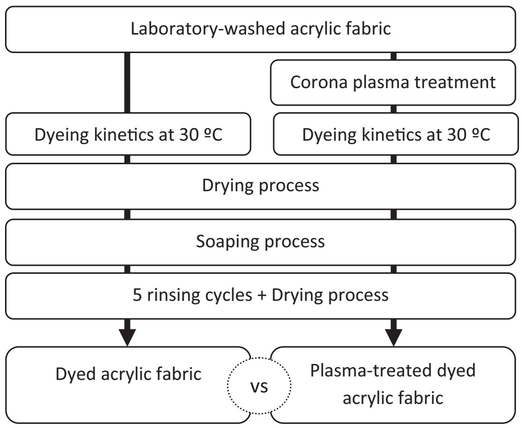

Fig. 4. Experimental process.

biodegradable surfactant easily soluble in cold water. It is stable versus water hardness agents, alkalis and acids as well as redox agents.

Drop test determinations are generally carried out if the water absorption time of the droplet is adequate (>5 s), according to the AATCC Test Method 39-1980. In this case, with laboratory-washed acrylic and corona plasma-treated fabrics, the absorption time of the water droplet was much lower, so the wettability was determined using glycerin as wetting liquid (analytical grade, *Panreac S.A.).*

2.2. *Experimental strategy*

2.2.1. *Experimental techniques*

2.2.1.1. Dyeing process and dyeing kinetics studies. The dyeing process was carried out with a *Mathis Colorstar* coupled with an on-line continuous measurement UV–visible spectrophotometer to follow and determine dyestuff concentration along all the experiment. The CI Basic Blue 3 dyestuff bath was prepared with a concentration of 50 mg/L in distilled water with 0.1% of glacial acetic acid. Temperature, liquid flow and volume conditions were kept constant at 30 °C, 1.0 L min^{-1} and 500 mL respectively. Bath relation was of 1/20 and pH value was monitored at 4.0, in all experiments.

2.2.1.2. Corona plasma treatment. Plasma treatments were carried out by means of an *Ahlbrandt FG-2* corona plasma using ambient air as plasma gas (Fig. 5). Distance between the electrodes was of 20 mm. Upper electrode size was of (400 × 20) mm. During the treatments, power, speed and incident current were kept constant

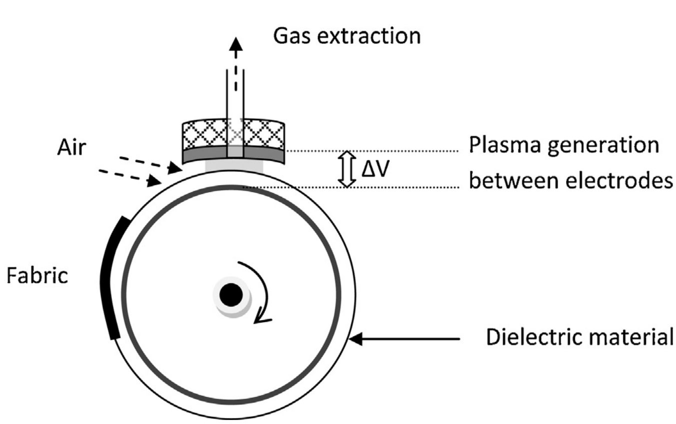

Fig. 5. Schematic of the corona plasma equipment used for acrylic fabric treatment.

at 380 W, 15 rpm and 1.90 A respectively. Fabrics were treated for 20 or 80 plasma sequences. Taking into account that each sequence corresponds to an exposition time of the sample to the plasma of 0.35 s, the treatment time of the acrylic fabrics corresponds respectively to 7 s and 28 s.

2.2.1.3. Washing, soaping and rinsing processes. Laboratory washing of the acrylic fabrics were carried out using an *Ahiba Polymat* equipment with a bath ratio of 1/10 of 5.0 g L^{-1} ECE standard detergent (ISO 105:C06) in distilled water solution. Working conditions were maintained constant (30 °C, 40 rpm) during the 30 min of the process. Samples were rinsed five times during 10 min at 30 °C in distilled water. Finally they were dried at 60 °C during 12 h followed by an over-drying at 105 °C during 15 min before their storage, in a desiccator.

Soaping process of the dyed samples was done in the same equipment, with a bath ratio 1/10 of 0.5 ml L^{-1} of *Laventin EE-BL* at 30 °C during 30 min. Rinsing and drying were done with the same procedure as described before.

2.2.1.4. X-ray photoelectron spectroscopy. X-ray Photoelectron Spectroscopy analysis were performed in XPS Spectrophotometer *TFA XPS* model, by *Physical Electronics Inc*. An Al monochromatic source of X-ray light with a power of 250 W was used. The relative error for XPS determination is about 0.5%. Each sample was analyzed at two different places and the average composition was calculated. In addition to the survey spectra, high-energy resolution spectra of characteristic peaks of C_{1s} elements are recorded through a narrow energy range. Spectra were referenced to the C_{1s} peak, at 284.80 eV.

2.2.1.5. Scanning electron microscopy (SEM). Topography of acrylic fibers was studied by Field-Emission Scanning Electron Microscopy using a *JEOL JSM-5000* SEM. All samples were Au coated prior to SEM observation. Observations were carried out at 10 kV working voltage.

2.2.1.6. Surface colorimetric analysis. The surface colorimetric analysis of the acrylic fabrics were performed in a *DataColor Spectraflash SF600 Plus-CT* spectrophotometer.

2.2.1.7. Drop test. Hydrophilicity of the acrylic fabrics was evaluated by determining the wetting time in seconds adapting the AATCC Test Method 39-1980 with glycerin instead of water. The test schematically consists of laying down a 10 μL droplet of glycerin on the surface of the fabric and measuring the time required for its complete absorption. Results are the average of at least four measurements.

2.2.1.8. UV–visible spectrophotometry. For the analysis of the concentration of dyestuff in the different aqueous baths, a *Shimadzu UV-1800 spectrophotometer* was used in fixed wavelength mode. For CI Basic Blue 3, the determination of the concentration was performed at the wavelength of 654 nm corresponding to the maximum absorption peak of the dyestuff.

3. Results and discussion

3.1. *Influence of plasma treatment on the surface properties of acrylic fabrics*

Fig. 6 shows SEM micrographs of the longest plasma treatment time evaluated in this work, as the striations observed are intrinsic to the fiber structure and can be readily observed on the untreated sample. The presence of finishing products (softeners, etc.) in the fiber surface (Fig. 6a) can be observed in the SEM images of the

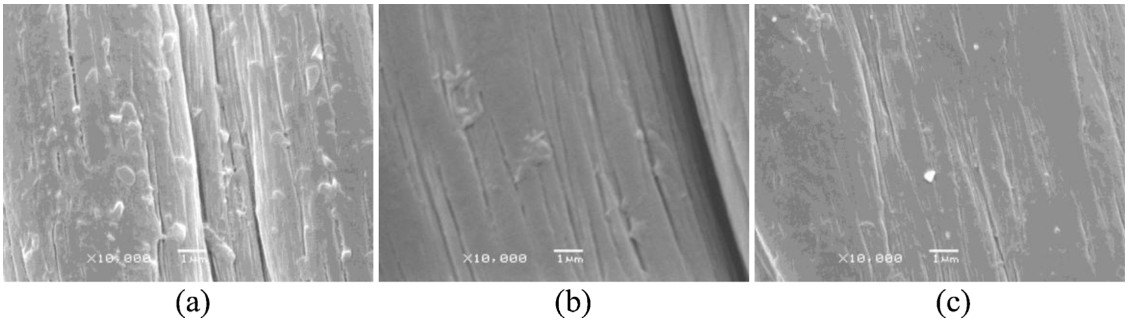

Fig. 6. Scanning electron micrographs of the acrylic fiber untreated fabrics (a) and after corona plasma treatment for 7 (b) and 28 s (c). Evidence of the effect of matter removal by plasma etching can be observed in (b) and (c).

Table 1
Glycerin droplet absorption time on acrylic fabrics.

	Untreated acrylic fabric	7 s plasma-treated acrylic fabric	28 s plasma-treated acrylic fabric
Glycerin droplet Absorption time (s)	70.0 ± 4.3	16.9 ± 2.7	9.3 ± 1.3

untreated acrylic fabric. It is clear that the laboratory washing process performed has not completely removed those finishing agents. Fig. 6b and c show that the plasma treatment produces a cleaning effect on the surface by etching a high percentage of this softener, increasing the etching effect with the treatment time. Moreover, it is important to notice that the microstructure of the fiber is not altered due to the plasma treatment performed.

As shown in Table 1, the absorption time of a droplet of glycerin on the acrylic fabric decreased 75.8% with a 7 s corona plasma treatment and 86.7% with a 28 s plasma treatment time as compared to the untreated acrylic fabric. This indicates a high improvement of the absorption time by the fiber surface by treating acrylic fibers with atmospheric air plasma.

In Table 2, the elemental composition of the surface is reported for untreated and 28 s corona plasma-treated acrylic fibers, the latter being selected for XPS for being the most extreme condition tested, and thus providing the highest differences with respect to the untreated fabric for the different parameters evaluated in this work. A decrease of 15.8% of C_{1s} proportion is observed for plasma-treated fabric compared to the untreated one as well as an increase of 10.7% of O_{1s} and of 3.6% of N_{1s} as a result of the plasma treatment, that allows, using air as plasma gas, to increase oxygen and nitrogen moieties, modifying the functionalization of the fiber surface.

The ratio of Si_{2p} on the fiber surface increases from 1.3% Si_{2p} for untreated fabrics, to 2.77% for the plasma-treated fabrics. During manufacture of the acrylic fiber, silicon compounds (softeners) are incorporated which are preferably located at the surface but also penetrate inside the macromolecular structure of the fiber by diffusion. With the laboratory washing of the fabrics, most of the products are eliminated from the surface. During the corona plasma treatment (28 s) of the fabrics, three effects may occur:

- Material etching of the acrylic fiber surface, as seen in Fig. 6b and also described in previous works [14,28], leading to surface cleaning in the first stages of treatment.
- Thermomigration of the silicone compounds from the outer layers of the fiber bulk to the surface due to localized heating as a consequence of surface recombination reactions of atoms from the plasma gas phase, which justifies the apparition of new Si atoms on the surface of the fiber.
- Surface functionalization by nitrogen and oxygen moieties.

Fig. 7 shows the C_{1s} high resolution XPS spectra of the untreated and 28 s corona plasma-treated acrylic fabrics. The surfaces of untreated and corona-plasma treated acrylic fibers (Fig. 7a) show three distinct peaks at 284.73 eV, 286.20 eV, and 288.14 eV, corresponding, respectively, to (—C—C,—CH), (—C—O,—C—N), and (—COOH) groups. Relative chemical bonds calculated from the relative area of each peak are reported in Table 3. Corona plasma treatment of the acrylic fabrics caused an increase of —CO and —CN groups, about 48%, as well as an increase of carboxylic groups in the surface of the acrylic fibers, whose relative ratio is doubled.

This increase is probably due to two simultaneous effects: cleaning of finishing agents by etching and surface functionalization of the acrylic fiber. The etching effect removes material from the surface, allowing that shielded functional groups remain active in the fiber surface. Besides, the surface functionalization as a result of plasma treatment provides additional groups on the acrylic fiber surface. These two effects lead to the increase of negatively ionizable groups on the fiber surface, as shown from Table 3, capable of offering new specific sites for establishing an ionic bond with the cationic dye molecules. As shown in Fig. 8, this produces higher adsorption speed of the cationic dye molecules on the surface of the fiber, and also reduces the migration speed of the dye from the specific sites of the fiber surface to the inside of the fiber due to the steric hindrance of the dyestuff molecules on the surface. Combined with the low dyeing process temperature performed (30 °C), this behavior inhibits the dye migration as well as the diffusion process on the inside of the macromolecular structure of the fiber.

Table 2
Elemental composition of untreated and plasma-treated acrylic fiber surface.

Element	Untreated	28 s-corona plasma treatment	Relative difference (%)
C_{1s}	76.87	61.03	−15.84
O_{1s}	12.30	23.03	+10.73
N_{1s}	9.60	13.17	+3.57
Si_{2p}	1.30	2.77	+1.47

Table 3
Fraction of carbon functional groups from high-resolution C_{1s} XPS peaks.

Sample	Relative chemical bonds (%)		
	284.80 eV	286.28 eV	288.14 eV
	C—C, C—H	C—O, C—N	—COOH
Untreated	70.56	28.15	1.29
28 s plasma treated	55.63	41.76	2.62

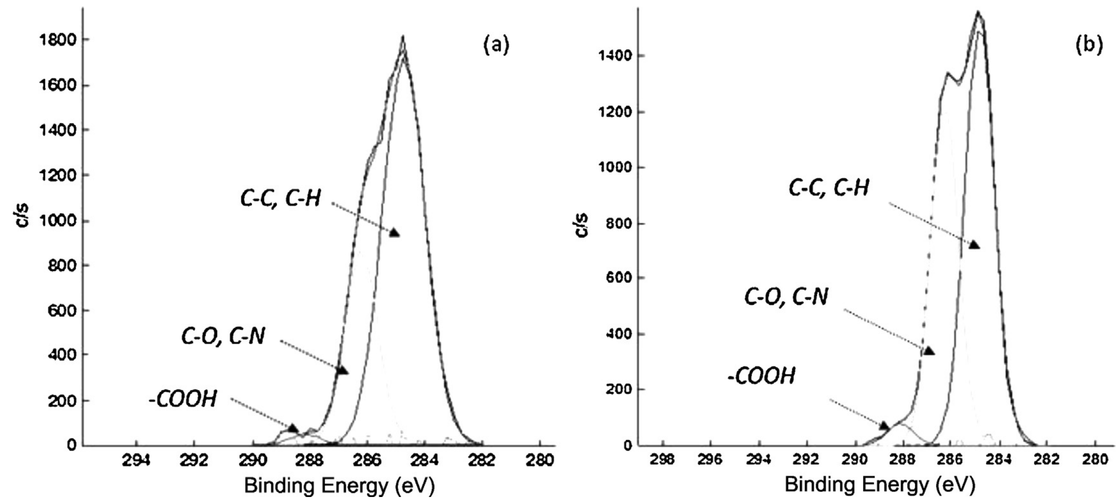

Fig. 7. C_{1s} high-resolution XPS spectra of the untreated (a) and 28 s corona plasma-treated (b) acrylic fabrics.

3.2. Dyeing kinetics of plasma-treated acrylic fabrics

Fig. 8 depicts the kinetics of the dyeing process at 30 °C during 18 h of untreated and plasma treated acrylic fabrics by the dyestuff (CI Basic Blue 3, 51004). The dyeing kinetics of the plasma-treated acrylic fabrics follow the same profile as the untreated one.

An initial concentration of dye in the dyebath of about 25 mg/L is sufficient to saturate the anionic groups on the acrylic fiber surface. In this study, the initial dye concentration is higher (50.0 mg/L), which ensures the diffusion model from a dye-saturated surface. The dyeing kinetics reflect (Fig. 8), an initial stage in the first minutes of the process, in which the cationic dye is adsorbed at high speed on the specific sites of the anionic fiber surface. Once the fiber surface is saturated by the dyestuff, the dye diffusion into the bulk of the fiber may be described by the Langmuir isotherm.

At the end of the dyeing process, plasma-treated acrylic fabrics absorb more amount of dyestuff than the fabrics that were not treated with plasma. The residual bath of the untreated acrylic fabric shows a percentage of exhaustion of the dyestuff of 64.4% after 18 h experiment when the residual bath of the 28 s plasma-treated fabric is of 55.6%; that is to say that the 28 s plasma-treated acrylic fabric absorbs a 24.72% more dyestuff than the untreated one. It can also be noticed that 7 s plasma-treated acrylic fibers have a higher exhaustion percentage of the residual bath (60.1% after 18 h dyeing process) than the untreated samples even if they are not reaching the highest exhaustion shown by the 28 s corona plasma treated acrylic fabrics.

The initial dyeing rates in the first 60 seconds of the dyeing process, presented in Fig. 9, are of 0.072%E/s (percentage of exhaustion per second) for the untreated fabric and 0.114%E/s for the 28 s plasma treated fabric, which corresponds to an increase of a 58.3% in the initial rate of dyeing due to the effects of corona plasma. It has also been observed that a shorter corona plasma treatment of 7 s of the acrylic fibers does not show any significant difference with the plasma-treated fabrics for longer times, regarding the initial rate of dyeing. The differences between both plasma treatment times are observed at longer dyeing times where the 28 s plasma treatment reaches a higher dyestuff exhaustion than the 7 second corona plasma treatment, as shown in Fig. 8. This behavior demonstrates that functionalization of the fiber surface and etching of finishing products by plasma treatment can be improved by a longer plasma treatment time.

Fig. 10 shows the dyeing speed at different time intervals of untreated and 28 s plasma-treated acrylic fibers during the dyeing process at 30 °C of the fabrics with CI Basic Blue 3 dyestuff. On the one hand, it can be observed that plasma-treated acrylic fabric shows a higher dyeing speed during the 18 h of the experiment, allowing to state that the dyestuff has a better affinity for the fiber

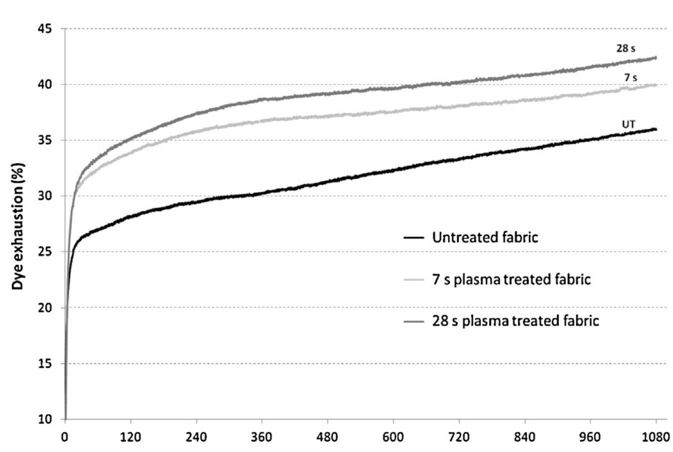

Fig. 8. Dyeing kinetics at 30 °C of untreated or corona-plasma treated acrylic fabrics.

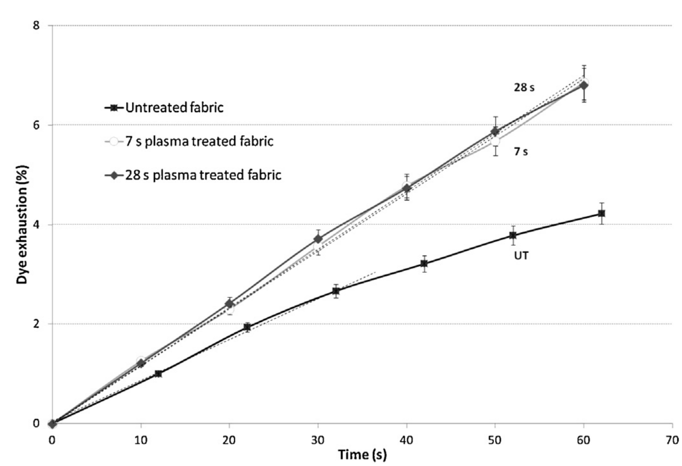

Fig. 9. Initial rates of dyeing in the first minute of dyeing process of untreated and corona plasma-treated acrylic fabrics.

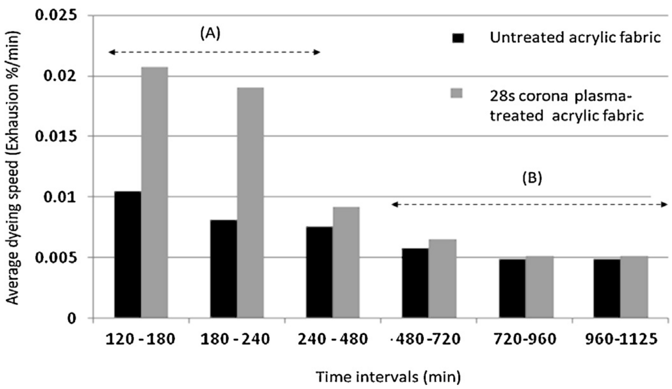

Fig. 10. Dyeing speed at 30 °C at different time intervals for untreated and 28 s corona plasma-treated acrylic fabrics.

surface which has been previously treated with plasma than for the untreated one. On the other hand, two clear phases in the dyeing process can be observed: in the first one (A), the more electronegative character of the surface of the plasma treated acrylic fabric causes an increased adsorption of the cationic dye on the surface which has a slow diffusion into the fiber at temperatures below the T_g temperature. In the second one (B), over 420 min of experiment, dyeing speeds of corona plasma-treated fibers tend to be equalized with the untreated ones, due to the fact that the concentration of anionic specific sites inside the fiber is the same in both cases due to the corona plasma treatment that only modifies the first nanometers of the surface of the acrylic fiber.

The CIE initial whiteness degree of the fabric is 73.96. The CIE whiteness degree of the 7 and 28 s-corona plasma treated fabric are 74.16 for both fabrics. This involves a variation of CIE whiteness degree due to the corona plasma treatment of 0.26%, which is not statistically significant, so it is concluded that the plasma treatments performed do not affect the degree of whiteness of the fabric.

Colorimetric analyses of the three dyed fabrics are presented in Fig. 11. Corona plasma treatment of the acrylic fabrics produces an increase of the $(K/S)_{corr}{}^{640\,nm}$ value respect to the untreated one of 3.5% and 8.8% for 7 s and 28 s plasma-treated fabrics respectively. This behavior gives a CIELab color difference between dyed with respect to the untreated fabrics of 1.29 and 1.49 for the 7 s and 28 s plasma treated fabrics, respectively. It has been verified by optical microscopy of transversal sections of the dyed fabrics (not shown) that at a temperature below the T_g of the fiber (30 °C), the diffusion of dye into the inside of the fiber is limited and may be described as annular dyeing.

As shown in Table 4, at the end of the dyeing kinetics, the difference between untreated and plasma-treated samples just dried and without any subsequent washing process is only of 1.3% and 3.2% respectively for 7 s and 28 s plasma-treated samples. However, after the washing process, these differences raise to 3.5% and 8.8% respectively, which demonstrates the increased fixation of the cationic dyestuff to the acrylic fiber as the result of the corona plasma treatment of the fabrics. Thus, colorimetric measurements show that previous plasma treatment of the fiber not only allows

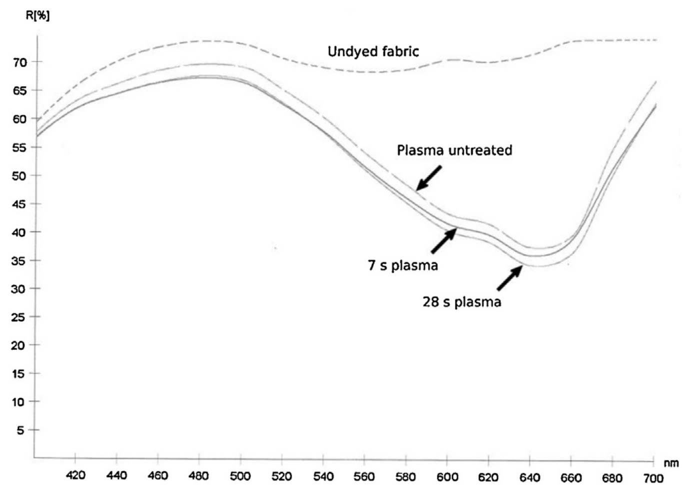

Fig. 11. Remission percentage spectra of untreated, 7 s, and 28 s plasma-treated acrylic fabrics as a function of the wavelength in the visible range.

increasing the exhaustion of the residual dyeing bath but also allows increasing the fixation of the dyestuff after conventional washing process.

The washing of the previously dyed acrylic fabrics was performed according to the experimental strategy (Fig. 4), and the resulting residual baths were kept to measure dyestuff concentration using the UV–visible spectrophotometer. For the determination of the concentration of CI Basic Blue 3 dyestuff in the bath, the analyses were performed at the wavelength of 654 nm corresponding to the maximum peak absorbance spectrum of the dye in the dispersion media. The results of the concentration of (CI Basic Blue 3; 51,004) dyestuff detached in the soaping residual baths correspond respectively to 0.0385, 0.0355 and 0.0343 mg of dyestuff released to the residual soaping bath per gram of acrylic fiber ($mg\,g^{-1}$), for untreated, 7 s and 28 s corona plasma-treated acrylic fabrics, respectively.

At the end of the washing process at 30 °C, untreated acrylic fabrics show a release of the dyestuff 10.9% higher than 28 s corona plasma-treated fabrics. This behavior means that in the case of plasma-treated fabrics the dyestuff tends to a better attachment with the acrylic fibers and allows concluding that corona plasma treatment not only achieves a higher exhaustion of residual bath by the acrylic fabric during the dyeing process but also facilitates the attachment of the cationic dye acrylic during the posterior washing process, allowing a lower release of the dyestuff. These results agree with the results obtained by colorimetric measurements and the determination of the percentage of remission of both fabrics.

Table 4
$(K/S)^{640\,nm}$ corrected values of acrylic fabrics dyed at 30 °C with and without plasma treatment.

Samples	$(K/S)^{640\,nm}$ Dyed and dried	$(K/S)^{640\,nm}$ Dyed, dried and washed sample
Untreated	0.79	0.50
7 s plasma-treated	0.81	0.52
28 s plasma-treated	0.82	0.54

4. Conclusions

Acrylic fabrics have been treated with corona plasma using air as plasma gas to evaluate its effects on surface properties and its relationship with dyeing with a cationic dye at low temperature, below the T_g of the fibers. Topographic analyses of the plasma-treated acrylic fibers showed that the treatment is eliminating the softeners used for the manufacture of the fibers by etching and can be considered as an additional preparation process to the conventional laboratory washing.

It has been shown that the air corona plasma used improves the surface wettability of the acrylic fabrics, related to a decrease of 15.8% of C_{1s} for plasma-treated fabric compared to the untreated one as well as an increase of 10.7% of O_{1s} and of 3.6% of N_{1s} as a result of the plasma treatment. It has been shown that the plasma treatment produces the modification of the physical and chemical surface properties of the fiber by three main effects working in synergy: the etching of silicon-based material from the acrylic fiber surface, plasma-thermomigration of the same finishing compounds, and the functionalization of the fiber surface by oxygen and nitrogen moieties.

The kinetics of the dyeing process at 30 °C during 18 h show that the dyeing kinetics follow the same trend for the plasma-treated acrylic fabrics and for the untreated one but the exhaustion of the dyebath reflects that the plasma-treated acrylic fabric absorbs a 24.7% more dyestuff than the untreated one. The initial rate in the first 60 s of the dyeing process follows an increase of a 58.3% in the initial rate of dyeing due to the improved wettability and access of the dyes to the fiber produced by the corona plasma treatment.

The plasma treatment performed does not affect the degree of whiteness of the fabric, and after dyeing with Basic Blue 3 there is increase of the $(K/S)_{corr}{}^{640\,nm}$ value of 3.5% and 8.8% for 7 s and 28 s plasma-treated fabrics, respectively with respect to the untreated one. This corresponds to a CIELab color difference between dyed plasma treated and untreated fabrics of 1.29 and 1.49 for 7 s and 28 s plasma treatment respectively. Untreated acrylic fabrics show a release of the dyestuff during the washing process at 30 °C a 10.9% higher than the 28 s corona plasma-treated fabrics. Therefore, in the plasma-treated fabrics the dyestuff shows a better attachment to the acrylic fibers. With selected dyestuff molecules, new techniques can be designed to amplify the knowledge about plasma-treated surface modifications of macromolecules.

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